Anorthite with Uvarovite Garnet Inclusions
含鈣鉻榴石包裹體的鈣長石

Kiran Kwon, JooSeong Moon, and Eun-Ah Jeong

Wooshin Gemological Institute of Korea (WGK)

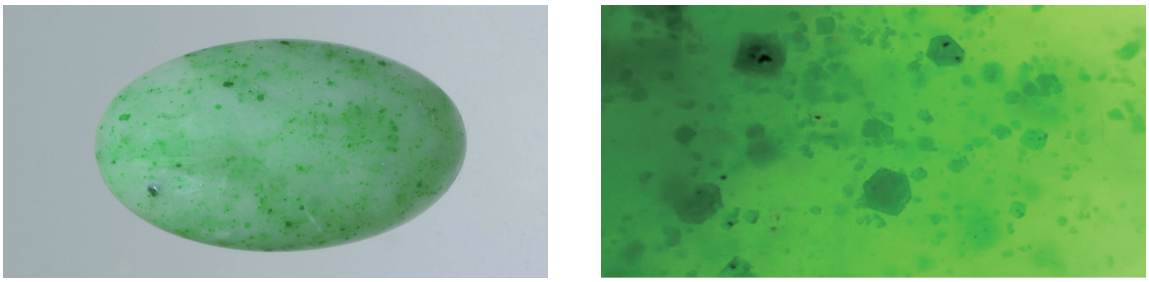

Fig. 1 The stone submitted for identification (left) and its green inclusions (right)

一塊由客戶所提供，被指為翡翠的綠色蛋面琢形寶石，經過Wooshin的一系列寶石檢測和鑑定分析後，結果顯示，該石是含鈣鉻榴石包裹體的鈣長石。

A green stone that we were told by the client was jadeite, was submitted to Wooshin for identification. A series of gemmology and analytical tests revealed that the stone was anorthite, which contained uvarovite garnet inclusions. It is presumed that a part of the rock with a uniform green colour was cut as a cabochon for a gem. The green colouration was due to the even distribution of green uvarovite inclusions. Uvarovite is usually found as small crystals deposited on the surface of chromite, but in this stone the garnet was uniquely distributed in the anorthosite.

The weight was 15.97cts and, though partly white, the overall colour was green with a scattering of dark green inclusions visible to the naked eye (Fig. 1). The refractive index was 1.56 (spot) and the specific gravity 2.75 (hydrostatic method), indicating that this test stone was not jadeite (RI: 1.64~1.65, SG: 3.30~3.36). It was inert to long wave ultraviolet (UV) light, but displayed red fluorescence under short wave, especially on green inclusions. Magnification testing (~60x) revealed that the host mineral was actually translucent white, while the overall green appearance was owing to the multiple dark green inclusions scattered throughout the stone. The inclusions were of various shapes such as hexagonal and irregular. Under transmitted light, they were emerald green, and their surface lustre was greater than that of the host.

To identify the green inclusions and the host material, various spectroscopic analyses were carried out. Fourier-transform infrared spectrometer (FTIR) and ultraviolet-visible (UV-Vis) spectroscopy were employed; however, due to the small size and distribution of the inclusions, the analyses were limited and satisfactory results were not obtained. Therefore, Raman microscopy and scanning electron microscopy-energy dispersive X-ray spectroscopy (SEM-EDS), which are capable of local area analysis, were used.

Raman spectra were collected using a Renishaw inVia Raman microscope. The laser excitations of 532 and 785nm, a laser focusing diameter of 2μm, and an objective lens of 50X were used. The measurement range was 100 to 3000cm^{-1}. Five spots on green inclusions exposed on the surface and another five spots on the white host were measured.

An SEM-EDS, FEI SEM (Inspect F) combined with EDS was used. With the permission of the client, the sample surface was polished with carbon powder and then plated with platinum. The accelerating voltage was 20KV. The same 5 spots on green inclusions and 5 spots on the white host as in the Raman analysis were measured. The measured elements were mapped over the area to see their distribution.

Analysis Results and Discussion

Raman microscopy

The green inclusions exhibited weak peaks at 178, 242 and 272cm^{-1} and strong peaks at 370, 529, 876 and 894cm^{-1} in the 150 to 900cm^{-1} range. Strong peaks were observed at 1125, 1320, 1371, 1483 and 1572, 1768, 1998 and 2197cm^{-1} in the 1000 to 2500cm^{-1} range. The peaks at 370, 529 and 876cm^{-1} are close to the 350, 550 and 900cm^{-1} of green garnets, which correspond to the rotational mode of the SiO_4 tetrahedra, the bending mode and stretching mode of Si-O, respectively. The positions of the peaks differ slightly depending on the type of green garnet (Table 1). Green garnets are represented by the chemical formula $Ca_3X_2(SiO_4)_3$, where Cr, Al and Fe are located at the X site, being classified as uvarovite, grossular, and andradite (demantoid), respectively. Some of the peaks in the 1000 to 2500cm^{-1} range were reported as peaks related to Nd^{3+}, a trace rare earth element contained in garnets [4].

The Raman spectra of the green inclusions were compared with those of demantoid, grossular, and uvarovite in the RRUFF database, referring to the reported Raman peaks (Table 1). The spectra of green inclusions matched that of uvarovite (Fig. 2).

Table 1 Major Raman peaks of green-series garnets (cm^{-1})

Uvarovite	Grossular	Andradite
178	186	174
242, 272	247, 280	236, 264
370	351, 373	312, 352, 370
459, 529, 590	529, 550	494, 516
876, 894	827, 848, 880	816, 842, 874

Kolesov and Geiger (1998)

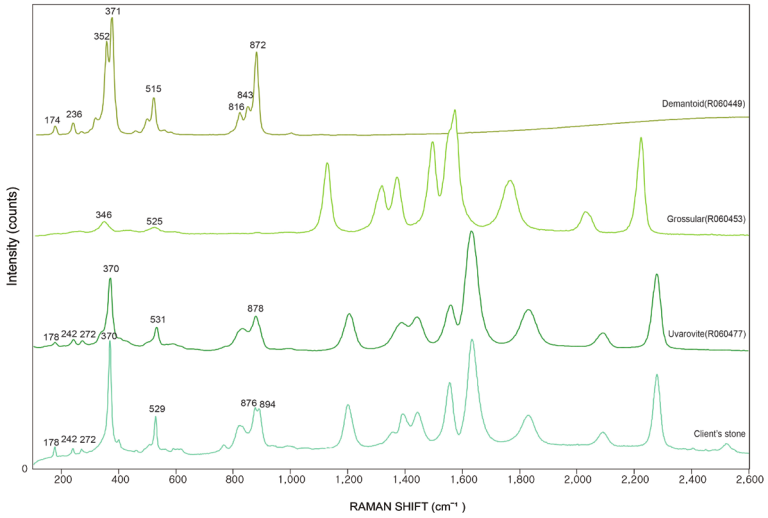

Fig. 2 Raman spectra of green-series garnets compared with that of a green inclusion (785nm Laser)

The host showed prominent peaks at 146, 198, 284cm^{-1}, strong peaks at 488, 504, 557cm^{-1}, and weak peaks at 684, 742, 764, 956, 985cm^{-1}. The strong peak at 504cm^{-1} is a peak that mainly appears in feldspar, which is attributed to the four-member rings of tetrahedra in the crystal. The feldspar group is made up of three end members, orthoclase ($KAlSi_3O_8$), albite ($NaAlSi_3O_8$), and anorthite ($CaAl_2Si_2O_8$), which are mixed to form solid solutions. Feldspar members were reported to have different peaks depending on their composition (Table 2).

When the Raman spectra of the host were compared with those of orthoclase, albite, and anorthite (RRUFF database), the spectra matched that of anorthite (Fig. 3).

Table 2 Major Raman peaks of end-member feldspars (cm^{-1})

Anorthite	Orthoclase	Albite
149, 178, 199	155, 176, 197	164, 185
248, 285, 325, 371	265, 282, 330, 370	291, 328
429, 488, 504, 557	454, 475, 513, 583	455, 480, 507
683, 745, 764	748, 810	762, 815
956, 984, 1020, 1077	988, 1036, 1098, 1123	977, 1097

J.J. Freeman et al. (2008)

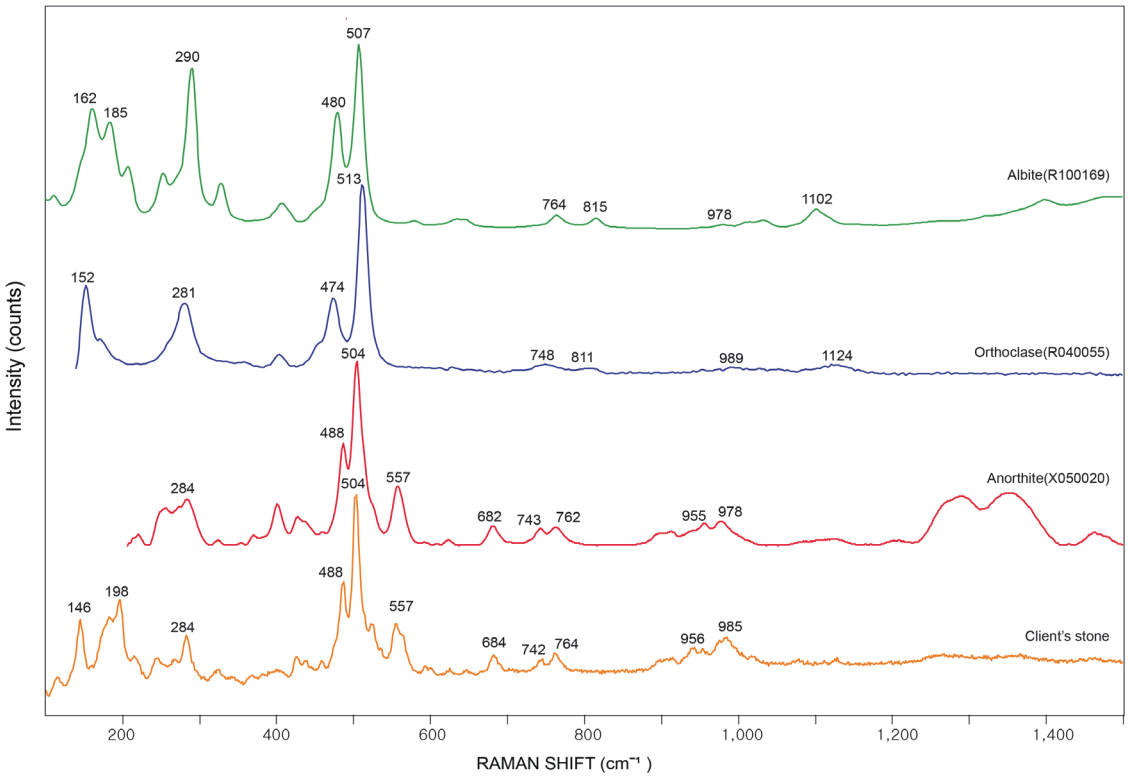

Fig. 3 Raman spectra of end-member feldspars compared with that of the host (785nm Laser)

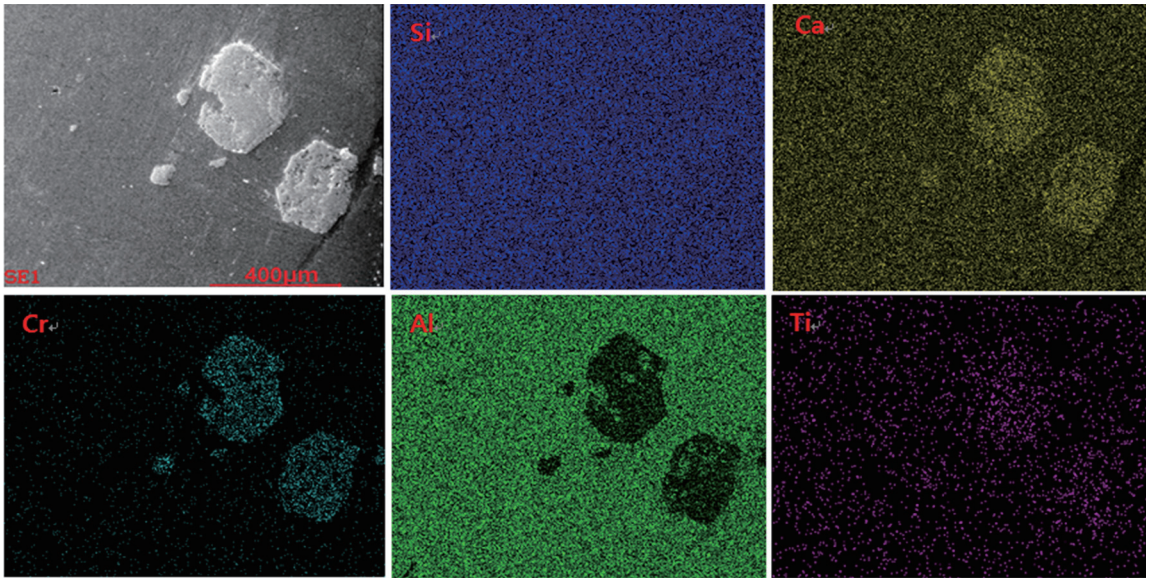

Fig. 4 Element mapping results of SEM-EDS

SEM-EDS

The size of green inclusions contained in the host varied from a small size of 10μm or less, to a large size of about 300μm. In order to obtain the element distribution data in the inclusions and the host, the element mapping of the measured elements was performed using SEM-EDS. Si, Cr and Ca were found in the green inclusions, where Cr and Ca were distributed more intensively than in the host. In addition, the partial distribution of Al was observed. In the host, Si, Al and Ca components were uniformly distributed and Ti was partially distributed (Fig. 4).

In the green inclusions, a large amount of SiO_2 and CaO were detected. In addition, 18wt% of Cr_2O_3 and 8wt% of Al_2O_3 were detected. A trace amount of TiO_2 was also detected at about 1wt% and Fe_2O_3 was below the detection limit. When the composition ratio of uvarovite and grossular was compared, uvarovite was dominant with a component of about 60mol%, while the grossular component was about 40mol%. In general, uvarovite contains not only pure chromium but also a considerable grossular component.

In the host, Al, Si and Ca were detected in large quantities. Small amounts of Na and Ti were detected in some parts of the test area, while K was not detected. The albite component (Na) detected at two sites was up to 8mol%. This is in the range of anorthite in petrology (albite component within 10%).

Conclusion

According to the analysis results, quoted above, the stone submitted to us for testing was identified as anorthite, containing uvarovite inclusions. Raman spectroscopic analysis is effective for the classification of the end members of green garnets and feldspar. However, since both are solid solutions, it is necessary to confirm the composition ratio for more accurate identification. There are many varieties of the plagioclase series including anorthite. In particular, it should be kept in mind that the ratio of albite components is similar to that of bytownite ($An_{90}Ab_{10}$ ~ $An_{70}Ab_{30}$), which is in the same plagioclase series.

References

[1] T. Moroz, A. Ragozin, D. Salikhov, G. Belikova, V. Puchkovb, and H. Kagi (2009). Micro-Raman spectra of ugrandite garnet, Spectrochim Acta A: Mol Biomol Spctrosc., Vol. 73, No. 3, pp. 436-439

[2] J.J. Freeman, A. Wang, K. Kuebler, B.L. Joliff, and L.A. Haskin (2008). Characterization of natural feldspars by Raman spectroscopy for future planetary exploration, The Canadian Mineralogist, Vol. 46, pp. 1477-1500

[3] B. Kolesov and C.A Geiger (1998). Raman Spectra of Silicate Garnets, Physics and Chemistry of Minerals, Vol. 25, No. 2, pp. 142-151

[4] R. Jasinevicius (2009). Characterization of vibrational and electronic features in the raman spectra of gem minerals, M.S. Thesis, pp. 49-67

[5] M.L. Frezzotti, F. Tecce, and A. Casagli (2012). Raman spectroscopy for fluid inclusion analysis, Journal of Geochemical Exploration, Vol. 112. pp. 1-20

[6] RRUFF project (http://rruff.info)